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COMPLETE SPECIFICATION

Lubricating Oil Composition

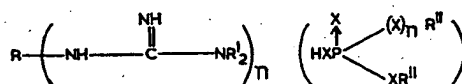
We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the Laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improved hydrocarbon lubricants and particularly to mineral lubricating oil compositions which possess good detergency, antiwear, as well as sludge-, corrosion- and rust-inhibiting properties.

Certain non-ash-forming polymeric nitrogen-containing compounds in which the nitrogen-containing groups may be amino or amido groups such as vinyl pyridines or vinyl pyrrolidones, function as detergents when added in small amounts to lubricants such as mineral lubricating oils. However, copolymers of that type have been found to lack wear-inhibiting properties and are corrosive, and under severe conditions of use such as under extreme temperatures and pressure they have been found to be shear-unstable resulting in sludging and other undesirable side effects.

The addition of basic polyvalent metal salts such as basic alkaline earth metal petroleum sulphonates or aromatic carboxylates such as alkyl salicylates imparts wear-inhibiting properties to lubricants containing the above-mentioned non-ash-forming detergents. However, it has been observed that the problem of corrosion remains and undesirable side effects such as sludging arise due to the apparent complexing tendencies between the nitrogen-containing polymer and the basic metal salts.

According to the present invention excellent ash-free detergent lubricants are provided having in addition wear- and corrosion-inhibiting properties as well as being resistant towards sludging tendencies, by adding to hydrocarbon lubricating oils such as mineral lubricating oils, containing polymeric nitrogen-containing detergents, a small amount of an oil-soluble hydrocarbyl-substituted or hydrocarbyloxy-substituted guanidine salt of an organic acid phosphate or phosphonate of a thio derivative thereof. The salt may be represented by the formula



(I)

wherein R is a hydrocarbyl or hydrocarbyloxy radical, e.g., an alkyl, aryl, aralkyl or alkaryl radical of from 6 to 18 carbon atoms or a corresponding oxy radical, R' is hydrogen or a C₁₋₄ radical, n is an integer of from 1 to 4, preferably one, X is oxygen or sulphur, preferably oxygen, and R'' is hydrogen or a radical containing hydrogen and carbon atoms, e.g. a C₁₋₁₈ alkyl or chloroalkyl radical, no more than one R'' being hydrogen.

The detergent nitrogen-containing polymers useful in compositions of the present invention include copolymers of monomers containing nitrogen-containing groups

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which may be amino or amido groups. They may be derived from monomers containing primary, secondary or tertiary (the latter two are preferred) amino nitrogen, including heterocyclic amino or amido nitrogen-containing substances, having an ethylenically unsaturated polymerizable group. These detergent polymers may be obtained by polymerizing vinyl-substituted heterocyclic nitrogen-containing substances such as vinyl pyridine, vinyl picoline and vinyl quinoline, vinyl pyrrolidone or vinyl arylamines such as para-aminostyrene, or polyamines prepared by reacting polymeric epoxy compounds with ammonia or primary or secondary amines, with polymerizable unsaturated alcohols, acids or esters such as acrylates and methacrylates of long chain fatty acids. The preferred polymeric amino or amido compounds are those containing tertiary amine groups and particularly those containing heterocyclic amino groups such as obtained by copolymerizing a polymerizable heterocyclic nitrogen base compound with a polymerizable unsaturated material free of heterocyclic nitrogen-containing radicals such as are described in British Patent Specifications 760,554 and 818,254. The copolymers include: copolymer of stearyl methacrylate and 2-methyl-5-vinyl pyridine; copolymer of stearyl methacrylate, lauryl methacrylate and 2-methyl-5-vinyl pyridine; and those which contain additional C_{1-4} alkyl methacrylates in the polymer, such as copolymers of stearyl methacrylate, lauryl methacrylate, methyl methacrylate and 2-methyl-5-vinyl pyridine; and similar copolymers in which the methyl methacrylate is replaced by butyl methacrylate and the 2-methyl-5-vinyl pyridine is replaced by 5-ethyl-2-vinyl pyridine; or copolymers of lauryl methacrylate and N-vinyl pyrrolidone or similar copolymers as described in British Patent 842,010 and British Patent 808,665, and mixtures thereof. Suitable acrylate-vinyl pyrrolidone copolymers are sold by Rohm and Haas (United States of America) under the designations Acryloid 315X or 917 or 966 and are copolymers of N-vinyl pyrrolidone and lauryl methacrylate of varying molecular weights. Other suitable polymeric amines are those available commercially such as those sold by E. I. du Pont de Nemours and Co. (United States of America) under the designations LOA 564 and 565, which are copolymers of lauryl methacrylate and diethylaminoethylmethacrylate (see United States Patent 2,737,496).

It is preferred that the polymeric detergents are copolymer of a vinyl pyridine and at least one alkyl acrylate having at least 8 carbon atoms in the alkyl group.

Particularly preferred detergent polymers are Acryloid 917 and 966 (copolymers of N-vinyl pyrrolidone and lauryl methacrylate in the molecular weight range of 400,000 to 500,000) or the copolymers of vinyl pyridine and mixtures of dissimilar methacrylate esters, the preparation of which is illustrated by the following examples.

EXAMPLE I

A mixture of 25% of 2-methyl-5-vinyl pyridine and 75% stearyl methacrylate was heated in a 50—50 mixture of benzene and a light mineral oil (East Texas 100 SSU at 100°F neutral) to about 120°C at which time 0.25% wt of ditert. butyl peroxide was added and the reaction mixture was maintained at this temperature for about 6 hours.

At the completion of the reaction the solvent was stripped off and the polymer diluted with neutral oil to a polymer content of about 30% by weight and filtered at 100—210°C. The copolymer had a molecular weight of about 200,000 and a nitrogen content of 2.94%.

EXAMPLE II.

30% Stearyl methacrylate, 51% lauryl methacrylate, 14% methyl methacrylate and 5.0% 2-methyl-5-vinyl pyridine were charged to a 300-gallon stainless steel autoclave. A 50—50 mixture of benzene and neutral petroleum oil was then added to the autoclave so as to furnish 1 part of the mixture per 3 parts of the total monomer. 0.25% of ditert. butyl peroxide was then added and the mixture heated at 120°C for about 7 hours.

At the completion of the reaction the benzene was stripped off to final conditions of 120°C and 10 mm Hg with nitrogen purging. The benzene-free product was then diluted with neutral oil to a polymer content of about 30% by weight and filtered at 100—120°C. The polymer had a molecular weight of about 600,000 and a nitrogen content of 0.54%.

The wear- and corrosion-inhibitors for the above detergents and represented by formula (I) include hydrocarbyl-substituted guanidine or polyguanidine salts of organic acid phosphates, phosphonates or the thio derivatives of said acids.

Examples of the guanidine compounds include decyl guanidine, dodecylguanidine, phenylguanidine, benzylguanidine, decylbiguanidine, decyloxyguanidine and mono-oleylamide of guanidine, as well as hydrocarbylguanidine carbonate and other suitable guanidine salts of inorganic acids.

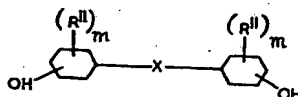
The acid portion of the salt includes hydrocarbyl acid phosphates, e.g., mono and dialkyl, mono and dicycloalkyl, diaralkyl, diaryl, alkyl aryl, aralkyl alkyl acid phosphates and their thio derivatives having from 8 to 30 carbon atoms in the molecule. Examples of suitable mono- and di-acid and/or thio acid phosphates are mono and distearyl acid phosphate, mono and dioleyl acid phosphate, mono and dicyclohexyl acid phosphate, dicresyl acid phosphate, lauryl cresyl acid phosphate, dibenzyl acid phosphate, lauryl benzyl acid phosphate, dilauryl acid dithiophosphate, dilauryl thio acid phosphate; alkyl acid phosphonates such as monobutyl chloromethyl phosphonate and monolauryl chloromethyl phosphonate. A preferred alkyl acid phosphate is "Lorol" ("LOROL" is a trade mark) acid phosphate, which is a mixture of phosphoric esters of "Lorol alcohol." The term "Lorol alcohol" is used in the trade to denote a mixture of primary normal aliphatic alcohols of 8 to 12 carbon atoms which are obtained by fractionation of the alcohols resulting from the reduction of coconut and/or palm kernel oils. "Lorol" acid phosphate mixtures are readily obtainable on the market and for this reason are preferred to the purified esters of greater scarcity and higher price. One "Lorol" acid phosphate type is sold under the trade name "Ortholeum 162" and is understood to be mainly a mixture of the mono and diacid phosphates of "lorol alcohol."

It is further preferred that the acid phosphate is a dilauryl phosphate or a mixture of mono and dilauryl phosphates.

Examples of oil-soluble guanidine salts are: (1) decyl guanidine dilauryl phosphate, (2) decyl guanidine dioleyl phosphate, (3) decyl guanidine distearyl phosphate, (4) phenyl guanidine dilauryl phosphate, (5) benzyl guanidine dilauryl phosphate, (6) decyl biguanidine dilauryl phosphate, (7) decyl guanidine distearyl phosphate, (8) decyl guanidine dilauryl dithiophosphate, (9) dodecyl guanidine dicresyl phosphate, (10) dodecyl guanidine monobutyl chloromethyl phosphonate and mixtures thereof.

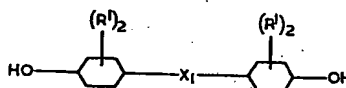
The present compositions may be improved with respect to their anti-corrosion properties by the addition of a minor proportion of an alcohol such as hexadecanol.

Additional improvement of oil compositions containing the above two additives of the present invention, namely the polymeric nitrogen-containing detergent and guanidine phosphate or phosphonate salts, particularly with respect to oxidation and storage stability is accomplished by addition of small amounts of alkylated bisphenols having the general formula:



(II)

where R^{II} is an alkyl radical containing up to 10 carbon atoms per molecule and m is zero or an integer from 1 to 4, at least one m being at least 1, the bisphenol preferably having the formula:



(III)

wherein in (II) X stands for $-S-$, $-S-S-$, Se , $-S-CH_2-$, $-CH_2-S-CH_2-$, $-CHR-$, $-CR_2-$, $-(CH_2)_n-$, $-NH-$, $-O-$, and wherein R stands for methyl or ethyl and n stands for an integer from 1 to 3 and wherein in (III) X_1 is CH_2 or sulphur and R^I is a tertiary alkyl radical. The most preferred alkylated bisphenols are represented by formula (III) those having a sulphur bridge or, and most especially, a methylene bridge and where R^I is tertiary butyl radical.

The alkylated bisphenols may contain from 1 to 8 alkyl groups, but preferably they contain from 2 to 6 alkyl groups. Alkylated bisphenols having 4 alkyl groups are particularly preferred. Each of the alkyl groups may contain from 1 to 10 carbon atoms, preferably 2 to 6 carbon atoms and especially 4 carbon atoms. Furthermore, the alkyl groups contained by any particular bisphenol may be the same or different and may be primary, secondary or tertiary alkyl groups. Bisphenols

containing at least one tertiary alkyl group are particularly preferred.

The alkylated bisphenol may be prepared by any of the methods known in the art of bisphenol manufacture, for example, by selecting the appropriate alkylated phenols as starting materials and condensing them together by any of the established methods. For example, alkylated bisphenols may be prepared by the method described in British Patent 806,961.

As examples of the alkylated bisphenols which may be used according to the invention there are mentioned bis(3-ethyl-4-hydroxyphenyl)disulphide, bis(3-methyl-4-propyl-5-hydroxyphenyl)disulphide, bis(2-isopropyl-3-butyl-5-hydroxyphenyl)selenide, 2,2'-diethyl-3-tertiary butyl-4,4'-dihydroxydiphenyl selenide, bis-1,2(2,6-ditertiary butyl-4-hydroxyphenyl)thiaethane, bis-1,2(2,5-diisopropyl-3-hydroxyphenyl)thiaethane, bis(3,5-ditertiary butyl-4-hydroxyphenyl)sulphide, 2,4-diisobutyl-3-hydroxybenzyl-2',4'-dipropyl-3-hydroxybenzyl sulphide, bis-1,2(3-octyl-5-tertiary butyl-4-hydroxyphenyl)ethane, bis-1,1(2,6-diisopropyl-4-hydroxyphenyl)ethane, 1,2-bis(2,4-ditertiary pentyl-3-hydroxyphenyl)propane, bis-2,2(4,5-ditertiary butyl-2-hydroxyphenyl)propane, bis(2-tertiary butyl-5-isopentyl-4-hydroxyphenyl)amine, bis(3,5-dibutyl-4-hydroxyphenyl)ether, bis(2,6-dipropyl-4-hydroxyphenyl)ether.

Preferred compounds are the alkylated bisphenols having a sulphur or methylene bridge, the former include bis(2,5-dipentyl-4-hydroxyphenyl)sulphide, bis(2,5-dihexyl-3-hydroxyphenyl)sulphide, bis(2-methyl-5-tertiary butyl-4-hydroxyphenyl)sulphide, bis(2-methyl-5-tertiary butyl-6-hydroxyphenyl)sulphide and particularly bis(3-tertiary butyl-5-methyl-2-hydroxyphenyl)sulphide, and examples of the latter, namely, alkylated bisphenols having a methylene bridge, include bis(2,3-ditertiary butyl-4-hydroxyphenyl)methane, bis(2,5-ditertiary butyl-4-hydroxyphenyl)methane, bis(2,6-ditertiary butyl-4-hydroxyphenyl)methane, bis(3,5-ditertiary octyl-4-hydroxyphenyl)methane, bis(3-tertiary butyl-5-tertiary octyl-4-hydroxyphenyl)methane, and especially bis(3,5-ditertiary butyl-4-hydroxyphenyl)methane.

Also the additive combination of the present invention appears to co-act with certain phosphorus compounds to give additional unexpected improvement in anti-wear and anti-scuffing. Thus, this desirable improvement can be imparted to lubricants of this invention by also incorporating a small amount of a partial or full ester of an organic phosphorus acid. Phosphorus compounds of this type include alkyl, cycloalkyl, alkaryl, aralkyl and aryl phosphites, phosphates, phosphonates, and their thio derivatives, such as C_{3-11} , alkyl phosphites, e.g., di and tributyl, octyl, lauryl, stearyl, cyclohexyl, benzyl, cresyl, phenyl phosphite or phosphates, as well as their thio derivatives; P_2S_5 -terpene reaction product, P_2S_5 -pine oil reaction product and metal salts thereof such as Na, K, Ca or Ba salts of P_2S_5 -terpene reaction product; dibutyl methane-phosphonate, dibutyl trichloromethane phosphonate, dibutyl monochloromethane phosphonate and dibutyl chlorobenzene phosphonate. The esters of pentavalent phosphorus acids such as diphenyl, dicresyl, triphenyl, tricresyl, trilauryl and tristearyl ortho phosphates, P_2S_5 -terpene reaction products and mixtures thereof are preferred.

Although from 0.01% up to 25% of each of the above-mentioned additives may be used, small proportions of each are in general sufficient for a highly effective combination. Thus the nitrogen-containing copolymer and the guanidine salt may be used in an amount of 0.110%, preferably 0.2—5%, each of the lubricant, while 0.05—2%, preferably 0.1—1%, of the bisphenol and 0.01—2%, preferably 0.1—1%, of an organic phosphorus compound, as described in the preceding paragraph (percentages being by weight) are highly useful.

The additive combinations of the present invention may be used to improve various hydrocarbon lubricating oils, whether of natural origin or synthetic, especially oils which are substantially paraffinic and/or naphthenic; they may contain substantial proportions of hydrocarbons having aromatic character but preferably the amounts and types of components are such that the viscosity index of the base oil is at least 80, preferably at least 90 to 150.

The oil may be derived from a highly paraffinic crude, in which case distillation and/or dewaxing may be sufficient to provide a suitable base stock; a minimum of chemical or selective solvent treatment may be used, if desired. Mixed base crudes and even highly aromatic crudes which contain paraffinic hydrocarbons also provide suitable oil base stocks by well-known refining techniques. Usually these comprise the separation of distillate fractions of suitable boiling range followed by selective solvent extraction with solvents such as furfural or phenol to provide raffinate fractions which are suitable for further refining by dewaxing and chemical treatment such as sulphuric acid treatment. Thus, it may be a refined hydrocarbon oil obtained from a paraffinic, saphthenic, asphaltic or mixed base crude, and/or mixtures thereof, such

as SAE 5W, 10W, 20W, 20, 30, 40, 50 mineral oils. The hydrocarbon oils may be blends of different mineral oil distillates and bright stock; they may have blended therewith minor but compatible proportions of fatty oils, such as castor oil or lard oil and/or synthetic lubricants, such as polymerized olefins, e.g., polyisobutylene.

5 The following compositions are representative of the invention, the percentages being by weight. 5

Composition A

Decyl guanidine dilauryl phosphate	1.4%
Copolymer of N-vinyl pyrrolidone/lauryl methacrylate (M.W. 600,000)	5.5%
Bis(3,5-ditert.butyl-4-hydroxyphenyl)-methane	0.5%
Mineral lubricating oil (SAE 30)	Balance

Composition B

Dodecyl guanidine dilauryl phosphate	1 %
Copolymer of N-vinyl pyrrolidone/lauryl methacrylate (M.W. 600,000)	5.5%
Bis(3,5-ditert.butyl-4-hydroxyphenyl)methane	0.5%
Mineral lubricating oil (SAE 30)	Balance

Composition C

Phenyl guanidine dilauryl phosphate	1.5%
Copolymer of N-vinyl pyrrolidone/lauryl methacrylate	5 %
Bis(3,5-ditert.butyl-4-hydroxyphenyl)methane	0.5%
Mineral lubricating oil (10W—30)	Balance

Composition D

Decyl guanidine dioleyl phosphate	1 %
Copolymer of Example II	5.5%
Mineral lubricating oil (SAE 20)	Balance

Composition E

Decyl guanidine dilauryl phosphate	1 %
Copolymer of N-vinyl pyrrolidone/lauryl methacrylate ("Acryloid 917" — Rohm and Haas)	5.5%
Bis(3,5-ditert.butyl-4-hydroxyphenyl)methane	0.5%
Tricresyl phosphate	0.8%
Dicresyl phosphate	0.4%
Mineral lubricating oil	Balance

Composition F

Decyl guanidine dilauryl phosphate	1 %
Copolymer of Example II	5.5%
Bis(3,5-ditert.butyl-4-hydroxyphenyl)methane	0.5%
Tricresyl phosphate	0.8%
Dicresyl phosphate	0.4%
Mineral lubricating oil	Balance

Composition G

Decyl guanidine dilauryl phosphate	2 %
Copolymer of Example II	5 %
Oleylguanidine amide	0.5%
Bis(3,5-ditert.butyl-4-hydroxyphenyl)methane	0.5%
Mineral lubricating oil	Balance

Other representative non-ash-forming lubricating compositions of the present invention include mineral oil containing:

- H — 25% copolymer of Example I + 0.5% of salt (4),
- I — 2% copolymer of Example II + 0.25% of salt (7),
- J — 5% of copolymer of stearyl methacrylate/lauryl methacrylate/
2-methyl-5-vinyl pyridine + 0.75% of salt (5),
- K — 4% of "Acryloid 917" copolymer + 0.5% salt (8) + 0.25%
bis (3-tert.butyl-5-methyl-2-hydroxyphenyl)sulphide,
- L — 5% "Acryloid 917" copolymer + 0.75% salt (10) + bis(2-
tert.butyl-5-methyl-2-hydroxyphenyl)methane.

In order to demonstrate the utility and improved properties of lubricating compositions of this invention, the compositions A and B were tested under L—4 engine test conditions and at the end of the test period the engine was clean and in perfect condition. Also these compositions passed the General Motor's MS Rust Test giving rating of 10 (perfect) and the Exhaust Gas Rust Test (EGRT) which comprises exposing oil-dipped steel panels to the exhaust vapours of a single cylinder 4-cycle Briggs (Briggs is a Trade Mark) and Stratton engine operating on a high sulphur fuel. The panels are exposed to the hot exhaust gases for 30 minutes, then cooled to a temperature of 0°F for 16 hours and allowed to warm to room temperature. The cycle is then repeated before inspection. These compositions (A and B) gave a rating of 10 (perfect). On the other hand a composition comprising mineral oil + 2% dilauryl acid phosphate and a composition comprising mineral oil + 1% decyl guanidine failed in the L—4 test, and in the MS and EGRT tests gave a rating of 4—6.

Lubricating compositions of this invention are particularly suitable for high temperature, high speed use as in aviation engines, automotive engines and truck engines, as well as industrial equipment operating under extreme conditions of temperature and pressure.

WHAT WE CLAIM IS:—

1. A lubricating composition comprising a major proportion of a hydrocarbon oil and minor proportions of a polymeric nitrogen-containing detergent and of an oil-soluble hydrocarbyl or hydrocarbyloxy guanidine salt of an organic acid phosphate or phosphonate or of a thio derivative thereof.

2. A composition as claimed in Claim 1, wherein the polymeric detergent contains amino or amido groups.

3. A composition as claimed in Claim 1 or Claim 2, wherein the polymeric detergent is a copolymer from a monomer containing heterocyclic nitrogen and a monomer free of heterocyclic nitrogen.

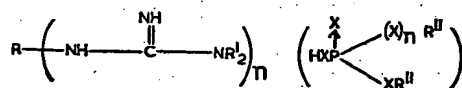
4. A composition as claimed in any of Claims 1 to 3, wherein the polymeric detergent is a copolymer of a vinyl pyridine and at least one alkyl acrylate having at least 8 carbon atoms in the alkyl group.

5. A composition as claimed in any of Claims 1 to 3, wherein the polymeric detergent is a copolymer of 2-methyl-5-vinyl pyridine and a mixture of lauryl and stearyl methacrylates.

6. A composition as claimed in any of Claims 1 to 3, wherein the polymeric detergent is a copolymer of 2-methyl-5-vinyl pyridine and a mixture of lauryl and stearyl and C_{1-4} alkyl methacrylates.

7. A composition as claimed in any of claims 1 to 3, wherein the polymeric detergent is a copolymer of vinyl pyrrolidone and lauryl methacrylate.

8. A composition as claimed in any one of Claims 1 to 7, wherein the guanidine salt has the formula



wherein R is a hydrocarbyl or a hydrocarbyloxy radical, R^1 is hydrogen or a C_{1-4} alkyl radical, n is an integer of from 1 to 4, X is oxygen or sulphur, and R^{11} is hydrogen or a radical containing hydrogen and carbon atoms, no more than one R^{11} being hydrogen.

9. A composition as claimed in Claim 8, wherein R is an alkyl or aryl radical of 6—18 carbon atoms, R^{11} is an alkyl or chloroalkyl radical of 1—18 carbon atoms, X is oxygen and n is 1.

10. A composition as claimed in any of Claims 1 to 9 wherein the acid phosphate is dilauryl phosphate or a mixture of mono and dilauryl phosphates.

11. A composition as claimed in any of Claims 1 to 10 wherein the guanidine salt is decyl- or phenyl guanidine dilauryl phosphate.

12. A composition as claimed in any of Claims 1 to 11 wherein the hydrocarbon oil is a mineral lubricating oil.

13. A composition as claimed in any of Claims 1 to 12, additionally containing a minor proportion of an alkylated bisphenol.

14. A composition as claimed in any of Claims 1 to 13, wherein each of the additives is present in a proportion of 0.01% to 25% by weight.

15. A composition as claimed in Claim 13, or in Claims 13 and 14, wherein the alkylated bisphenol is present in a proportion of 0.05 to 2% by weight.

16. A composition as claimed in any of Claims 1 to 15 additionally containing a minor proportion of a partial or full ester of an organic phosphorus acid.

17. A composition as claimed in Claim 16, wherein the ester of an organic phosphorus acid is present in a proportion of 0.01 to 2% by weight.

18. A composition as claimed in any one of Claims 1 to 17 wherein the polymeric detergent and the guanidine salt each are present in a proportion of 0.1 to 10% by weight.

19. A hydrocarbon lubricating composition substantially as hereinbefore described as any of Compositions A to L.

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